SCIENCE FOR CERAMICS PRODUCTION

A THERMOSTABLE COMPOSITE CERAMIC BASED ON CORDIERITE

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A porous, thermostable composite material was developed from natural powders that form a cordierite matrix on sintering and a filler — fibrous nanostructure aluminum oxide powder with high porosity and reactivity. It was found that incorporation of the nanocrystalline aluminum oxide filler in the composite with the cordierite matrix causes the formation of a polyporous structure that increases the porosity and thermal stability and improves the heat-insulating properties of the material.

Porous thermostable ceramic materials with low TCLE are required for fabricating refractories, thermal insulation, catalyst supports, and filters for hot liquids and gases used in industry [1, 2]. One of these materials is a cordierite-based ceramic. However, in addition to the valuable physicomechanical properties, cordierite has a drawback — a narrow temperature range of existence, as it decomposes into mullite and other silicate compounds at temperatures above 1420 – 1450°C, and this has led to a search for ways of obtaining cordierite at low sintering temperatures by activating the initial components (US Patent No. 532282) [3] or by adding modifiers. Since the thermal stability of ceramic articles is a function of the composition, pore structure, and TCLE of the material, components which form a ceramic with a low TCLE on sintering are selected as the initial substances and blowing agents are incorporated as additives [4, 5]. In other cases, polydisperse powders are used to form uniform slit pores in the ceramic for fabricating porous thermostable materials. However, this method does not result in formation of a highly porous and strong material [6].

We wanted to obtain a porous thermostable composite made of natural minerals and industrial powders that form a cordierite matrix on sintering, to use fibrous nanocrystalline aluminum oxide powder with high reactivity as the modifying filler, and to study the structure, thermophysical, and physicomechanical properties of the composite.

A charge of Granitik-Vesko clay from the Veselovskoe deposit, talc from the Onotsk deposit, and industrial alumina in the ratio of components that corresponds to the composition of cordierite was prepared for fabricating the cordierite matrix. Fibrous nanocrystalline aluminum oxide powder with the structure of α-corundum, ground and passed through a 0.08 mm sieve was used as the filler; it was a finely disperse white substance with particles 10 – 15 μm long and 3 – 5 μm in diameter. The powder particles consisted of 40 – 45 nm nanograins of aluminum oxide. The bulk density of the powder was 510 kg/m^3, the pycnometric density was 3750 kg/m^3, and the specific surface area was 43 m^2/g.

The oxide fibers used to make the powder were synthesized by saturating hydrated cellulose powder with an aqueous solution of aluminum chloride followed by drying and heat treatment conducted in special conditions. Water and organic products of thermolysis of the polymer were removed during heat treatment, the salts homogeneously distributed in the cellulose chain were dissociated, and γ-aluminum oxide grains measuring 4 – 6 nm were formed in the 600 – 700°C temperature region. Structural transformations of Al_2O_3 took place, particle growth was observed with an increase in the temperature, and this allowed regulating their size and crystal structure by altering the conditions of synthesis [7]. The oxide fibers obtained, consisting of grains of α-Al_2O_3, were ground in a drum with porcelain balls and screened by fractions.

The composite samples were made according to traditional ceramics technology: blanks were molded from a powdered mass of the initial components by semidry molding at a pressure of 12 MPa and dried at 100 ± 5°C. The samples were isothermally fired in an electric furnace in the 1250 – 1400°C temperature range with a 50°C interval.

The crystal and pore structure of the sintered samples was investigated by x-ray phase and electron-microscopic

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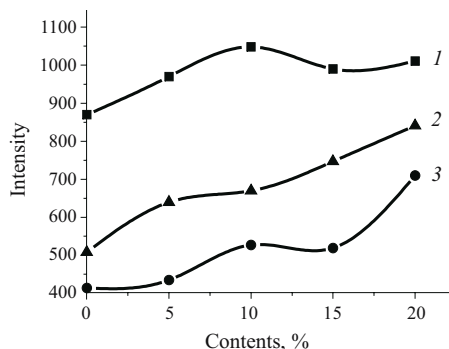
Fig. 1. Integral intensity of reflections as a function of filler content in samples of composites fired at 1300°C. Reflections: *1*) cordierite (511); *2*) aluminum oxide (012); *3*) spinel (400).

Fig. 2. Microstructure of filler powder (*a*); fragment of a fiber consisting of nanograins of aluminum oxide (*b*); cordierite matrix (*c*) and composite with fibrous filler (*d*).

analysis. The physicomechanical and thermal properties of the samples of matrix and composites (density, porosity, compressive strength, thermal conductivity, TCLE, and thermal stability) were determined by standard methods. In studying the nanocrystalline filler, x-ray structural analysis and high-resolution scanning and transmission electron microscopy were used in studying the nanocrystalline filler.

Solid-phase reactions and phase transitions took place in sintering samples of the materials in the ceramic composites. The study of the phase composition of the products of reaction of the components with the initial matrix fired at 1100°C showed that enstatite, aluminum silicate, and aluminomagnesium spinel formed in it. Silicon oxide was present in the α-quartz and β-cristobalite phases, and the alumina retained the initial α-corundum structure. When the α-Al_3O_3 nanocrystalline filler was incorporated in the matrix while heating the composites to 1200 – 1250°C, it reacted with the enstatite, so that the enstatite content decreased and the concentration of aluminomagnesium spinel increased. Moreover, the added Al_2O_3 filler reacted with the excess silicon oxide, forming an additional mullite phase. At temperatures above 1250°C, a solid-phase reaction actively took place with formation of cordierite, and α-corundum, aluminomagnesium spinel, mullite, α-quartz, and β-cristobalite were present as impurities. When the filler content in the composite was increased to 20%,[2] the proportion of aluminomagnesium spinel increased due to reaction of the nanocrystalline aluminum oxide with magnesium oxide, and the integral intensity of the reflections of the basic phase — cordierite — increased due to an increase in its content in the material (Fig. 1).

The study of samples of the matrix by electron microscopy showed that the cordierite ceramic consisted of sintered round particles with a large number of 4 – 10-μm pores and inclusions of small oval particles and elongated parallelepipeds concentrated in cavities and macropores in the ceramic. The added nanocrystalline aluminum oxide powder decreased the heterogeneity of the material by occupying va-
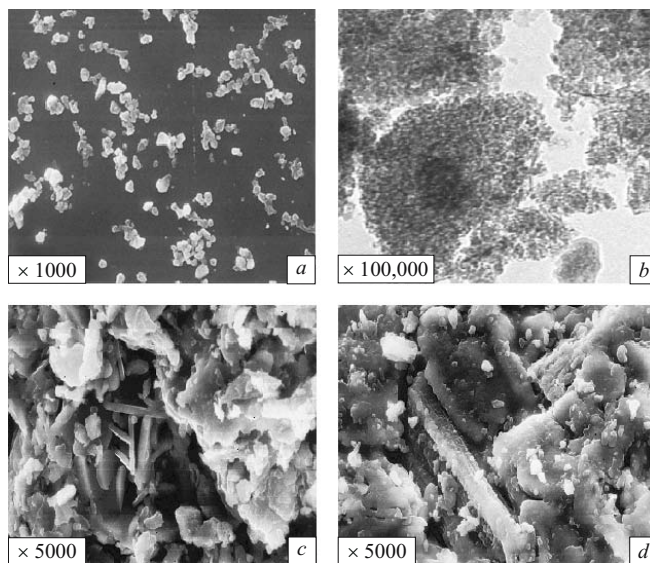
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[2] Here and below: mass content.

cancies and macropores in the cordierite matrix. Small particles were located between and on the surface of the fibers (Fig. 2). Due to the features of the nanostructure and high reactivity of the filler, solid-phase reactions took place on contact with the matrix and chemical compounds formed on the surface of the fiber particles, which strengthened the contacts between components in the composite and increased the thermal stability of the material with a simultaneous increase in its porosity.

The change in the microstructure and phase composition of the composite material with an increase in the filler content and heat treatment temperature significantly affected the physicomechanical and thermophysical properties of the composites. Determination of the density and porosity showed that a fibrous skeleton formed with an increase in the nanocrystalline filler content, so that the porosity increased and the density of the composites obtained decreased.

The samples containing a filler had developed, permeable, communicating pores. The porosity of the samples of matrix and composite with a 20% filler content fired at 1250°C was 4.0 and 30.7%, and their apparent density was equal to 2.3×10^3 and 1.9×10^3 kg/m³. The change in the porosity and apparent density of the samples with an increase in the heat treatment temperature from 1200 to 1400°C took place nonmonotonically. This was due to the following processes that took place in the material.

Sintering the samples activated transfer of matter for all compositions due to development of diffusion processes, and this caused formation of cordierite and increased the density of the material. In addition, at 1300°C, the silicates in impurities in the clay melted, which caused viscous flow of the material and closing of small pores, so that the porosity decreased and the density of the composite samples increased.
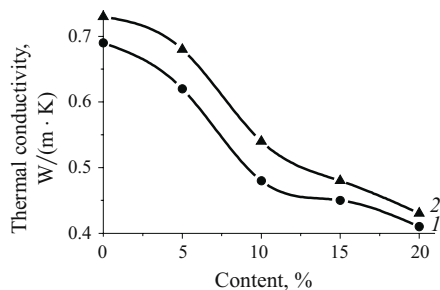
Fig. 3. Thermal conductivity of composite samples as a function of content of α-Al_2O_3 filler fired at 1300°C (*1*) and 1350°C (*2*); measurement temperature of 200°C.

Increasing the temperature to 1400°C caused partial decomposition of low-melting silicates, which increased the porosity of the composites. As a result, the open porosity of the material with 20% filler fired at 1300°C was 19.5%, the apparent density was 2.18×10^3 kg/m³, and after firing at 1400°C, these characteristics were respectively equal to 22.3% and 2.08×10^3 kg/m³. It should be noted that at 1400°C, the cordierite matrix with no filler decomposed with formation of mullite and low-melting aluminosilicates, and the samples lost their shape and melted. The nanocrystalline aluminum oxide powder filler increased not only the porosity, but also the refractoriness of the material. The composite samples retained their shape, and the material did not crack.

The composition, pore, and crystal structure determine the thermophysical properties of heat insulators. According to the theory of thermal conductivity, highly porous ceramic materials can be considered as systems that consist of a solid substance that forms walls between pores (skeleton) and air that fills the pores. When the proportion of filler in the composite increased, the thermal conductivity of the samples decreased in a narrow sintering temperature range, since the degree of scattering of thermal phonons in the polyporous structure formed in the material increased (Fig. 3).

The TCLE of the technical ceramic characterizes the thermal stability and lifetime of articles. Addition of a nanocrystalline fibrous filler caused a slight increase in TCLE due to an increase in the content of aluminum oxide introduced by the filler, which has a higher CLTE (8×10^{-6} K^{-1}) than cordierite (Fig. 4a). It should be noted that when the sintering temperature was increased from 1250 to 1400°C, the CLTE for all compositions decreased (Fig. 4b) due to formation of cordierite in the composite, and the temperature region of its existence was within the limits of 1300 – 1410°C [8].

The polyporous structure formed as a result of solid-phase reactions, formation of chemical compounds at filler and matrix contact sites, and melting and decomposition of low-melting impurities in the composite had the basic effect on the strength characteristics of the materials. The strength indexes of the cordierite matrix decreased with an increase in the temperature, since the initial clay powder contained
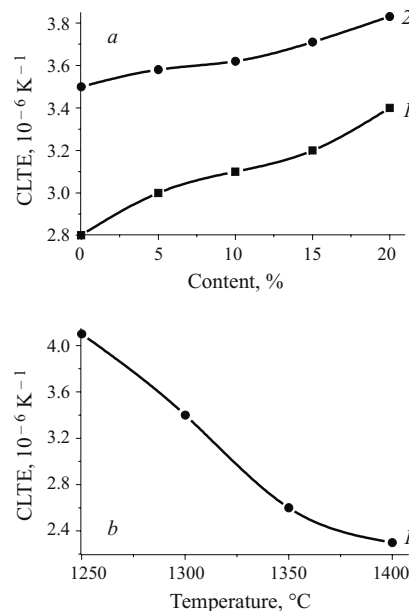

Fig. 4. TCLE of composite ceramic fired at 1300°C as a function of filler content (*a*) and heat-treatment temperature of composite containing 20% filler (*b*): *1* and *2*) TCLE at 400 and 800°C, respectively.

quartz and alkali and alkaline-earth oxides in the amount of 2.5 – 3.0%, as well as kaolinite, as impurities. These impurities did not have a significant effect at a firing temperature of 1200 – 1250°C, but when the temperature was increased, the low-melting silicates formed caused fusion of the material.

Similar complex dependences of the compressive strength of composites fired in the 1250 – 1400°C temperature range on the filler content and heat treatment temperature were established. The low strength of the samples fired at 1300°C was due to formation of the glass phase of alkali and alkaline-earth silicates, which caused the matrix of the composite to become more brittle. Addition of the filler and increasing the heat treatment temperature to 1350 – 1400°C strengthened the material, since solid-phase reactions of formation of cordierite in the matrix took place in this temperature region, low-melting silicates were degraded, and spinel links formed on the fiber–matrix boundary. The maximum values of the strength of the materials were attained at a firing temperature of 1350°C and filling of the matrix with nanocrystalline aluminum oxide in the amount of 15 – 20%. Increasing the temperature to 1400°C slightly decreased the strength indexes of the samples due to the increasing open porosity of the composites (Fig. 5). The fibrous aluminum oxide particles added not only participated in solid-phase process of formation of high-melting compounds but also served as energy dissipation centers for crack formation and growth in fracture of the composites.

The study of the thermal stability of the composite ceramic confirmed its high resistance to thermal shock. Samples of the composites were heated to 800°C, held in the fur-
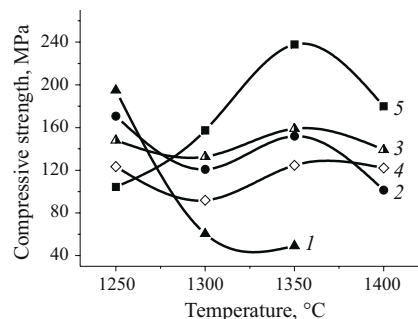
Fig. 5. Compressive strength of ceramic samples as a function of temperature of heat treatment of matrix (*1*) and composites with filler content of 5% (*2*), 10% (*3*), 15% (*4*), and 20% (*5*).

nace for 30 min, and then rapidly immersed in a vessel with running water (10°C). The studies showed that the color, shape, and size of the samples did not change no cracks appeared, and the composites withstood 1000 heating and cooling cycles without fracture of the material.

When nanocrystalline aluminum oxide filler was added to the cordierite matrix in the composite, solid-phase reactions thus took place on the matrix–filler boundary, and this increased the strength and thermal stability of the material. In addition, incorporation of the nanostructure filler caused the formation of a polyporous structure that increased the porosity and thermal stability and improved the heat-insulating

properties of the material. The ceramic obtained withstands repeated temperature changes, has TCLE of $3.5 \times 10^{-6}\,K^{-1}$, and can be used as flame shields, lining for resistance furnaces, and for inductor parts.

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